Kinetics of U(VI) reduction control kinetics of U(IV) reoxidation

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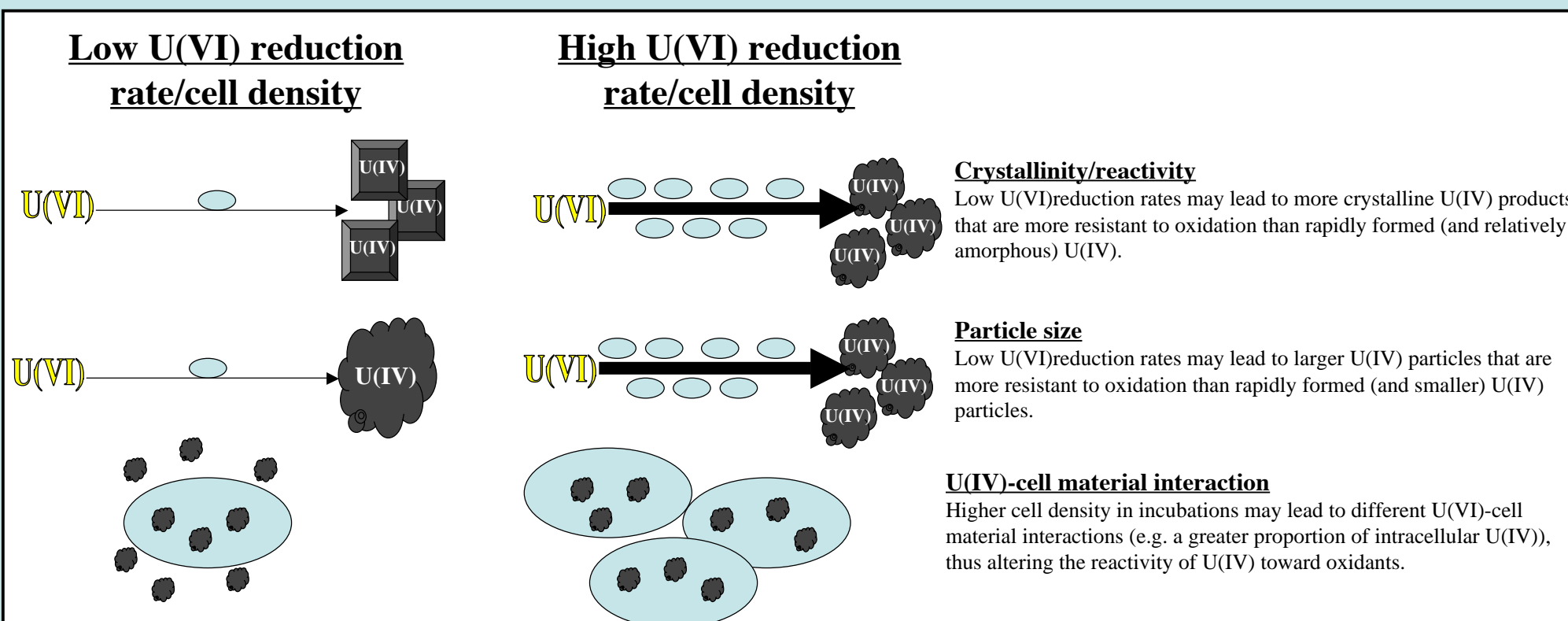[1]Department of Civil and Environmental Engineering, The Pennsylvania State University

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Introduction

For the in situ reductive immobilization of U to be an acceptable strategy for the removal of that element from groundwater, the long-term stability of U(IV) must be determined. Rates of biotransformation of Fe species influence the mineralogy of the resulting products (Fredrickson et al., 2003; Senko et al., 2005), and we hypothesize that the rate of U(VI) reduction influences the mineralogy of resultant U(IV) precipitates. We hypothesize that slower rates of U(VI) reduction will yield U(IV) phases that are more resistant to reoxidation, and will therefore be more stable upon cessation of electron donor addition. U(IV) phases formed by relatively slow reduction may be more crystalline or larger in comparison to their relatively rapidly-formed counterparts (Figure 1), thus limiting the reactivity of slowly-formed U(IV) phases toward various oxidants. The physical location of U(IV) precipitates relative to bacterial cells may also limit the reactivity of biogenic U(IV) phases. In this situation, we expect that precipitation of U(IV) within the bacterial cell may protect U(IV) from reoxidation by limiting physical contact between U(IV) and oxidants (Figure 1). We assessed the effect of U(VI) reduction rate on the subsequent reoxidation of biogenic U(IV) and are currently conducting column scale studies to determine whether U(VI) reduction rate can be manipulated by varying the electron donor concentration used to stimulate U(VI) reduction.

Figure 1. Hypothesized bioreduction rate-dependent differences in U(IV) products

Crystallinity/reactivity
Low U(VI) reduction rates may lead to more crystalline U(IV) products that are more resistant to oxidation than rapidly formed (and relatively amorphous) U(IV).

Particle size
Low U(VI) reduction rates may lead to larger U(IV) particles that are more resistant to oxidation than rapidly formed (and smaller) U(IV) particles.

U(IV)-cell material interaction
Higher cell density in incubations may lead to different U(VI)-cell material interactions (e.g. a greater proportion of intracellular U(IV)), thus altering the reactivity of U(IV) toward oxidants.
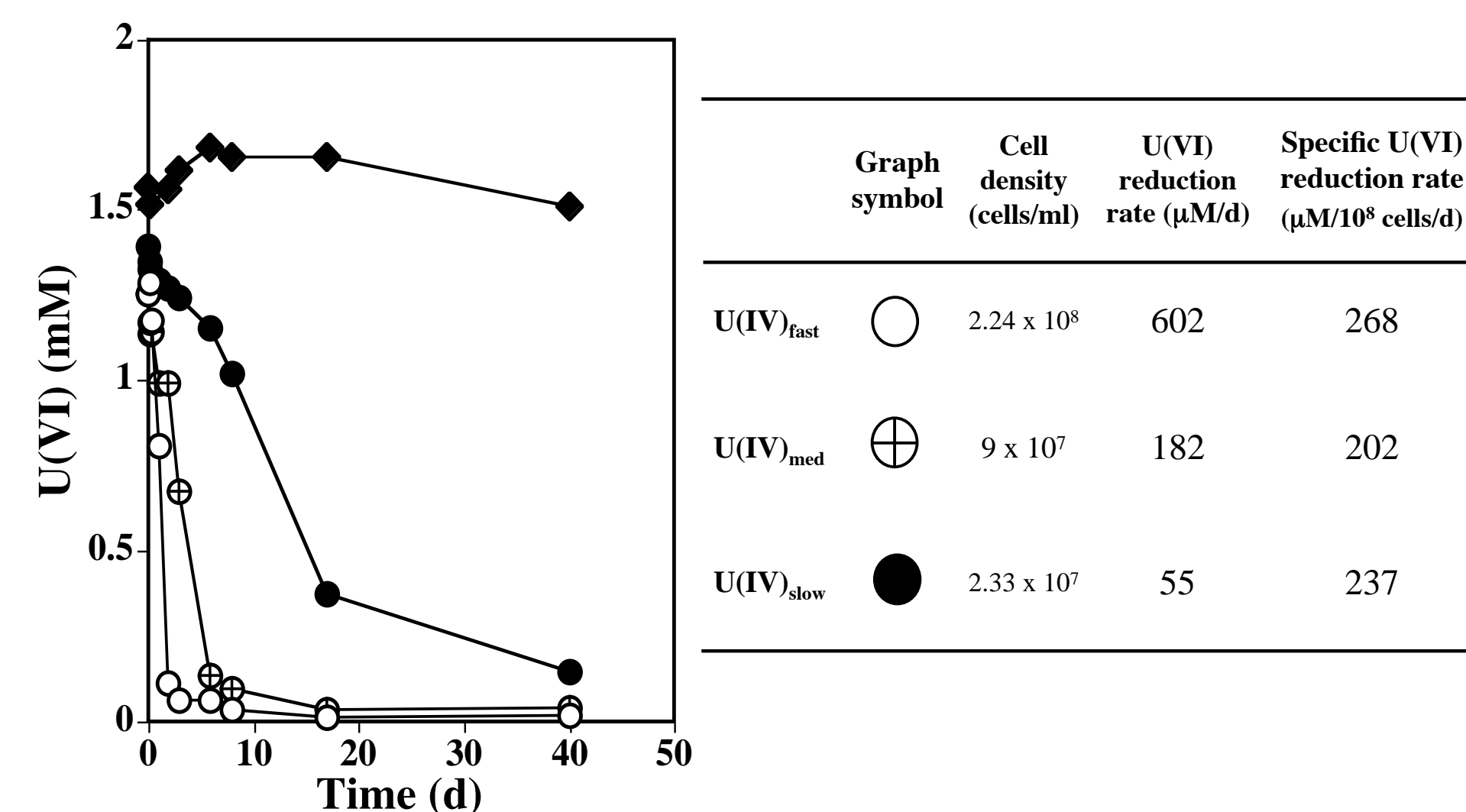
The effect of U(VI) bioreduction rate on the subsequent reoxidation of biogenic U(IV)

Preparation of U(IV) via different rates of bioreduction

-Resting cells of *Shewanella putrefaciens* CN32 were incubated in bicarbonate-buffered (2.5 g/l, pH 6.8) medium containing 1 mM uranyl actate and 5 mM sodium lactate.

-Rates of U(VI) reduction were manipulated by varying the cell density in each incubation (Figure 2).

Figure 2. Bioreduction of U(VI) by various cell densities of *S. putrefaciens* CN32

Graph symbol	Cell density (cells/ml)	U(VI) reduction rate (μM/d)	Specific U(VI) reduction rate (μM/10⁸ cells/d)
U(IV)$_{fast}$ (○)	2.24×10^8	602	268
U(IV)$_{med}$ (⊕)	9×10^7	182	202
U(IV)$_{slow}$ (●)	2.33×10^7	55	237

Visual characteristics of biogenic U(IV)

Figure 3. Differences in color of U(VI)-reducing incubations after complete reduction of U(VI)
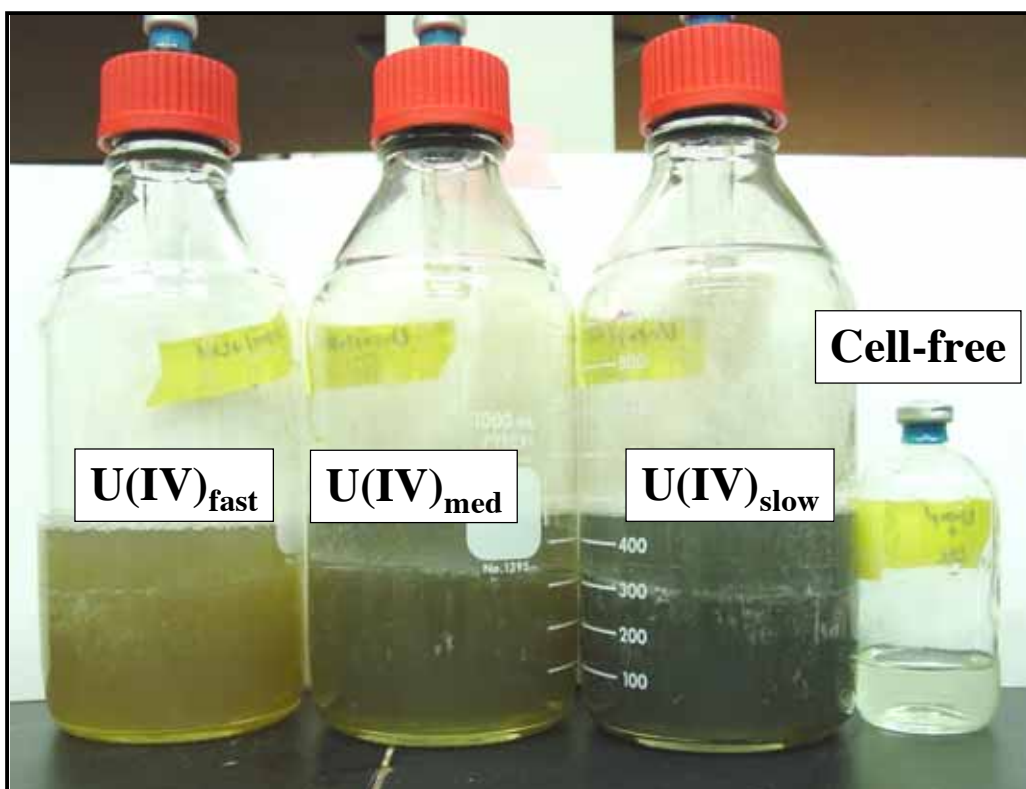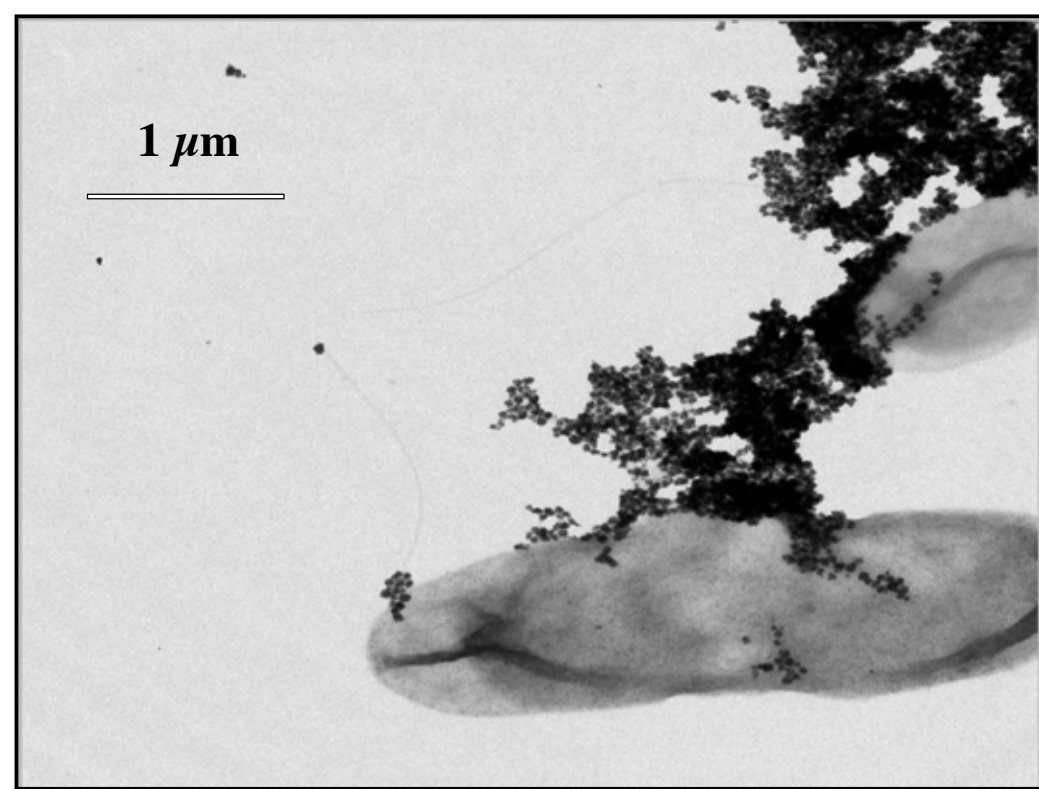

Figure 4. Transmission electron micrograph of negatively stained *S. putrefaciens* after complete reduction of U(VI). Cell density used for bioreduction was 1 x 10⁸ cell/ml.

Results and Discussion

-U(IV)$_{fast}$, U(IV)$_{med}$, and U(IV)$_{slow}$-containing incubations exhibited different colors after complete reduction of U(VI) (Figure 3).
-May be attributed to differences in U(IV) mineralogy or simply to the differences in cell density of each incubation.
-Biogenic U(IV) deposited extracellularly (Figure 4).
-Not clear if this occurs in all incubations.
-Relatively rapidly-formed U(IV) was correspondingly more susceptible to biological and abiotic oxidation coupled to reduction of a variety of oxidants (Figure 5).

Oxidation of biogenic U(IV) by various oxidants

Cell suspensions containing U(IV)$_{fast}$, U(IV)$_{med}$, and U(IV)$_{slow}$ were pasteurized and added to bicarbonate buffer (2.5 g/l, pH 6.8) amended with various oxidants.

Figure 5. Biological and abiotic oxidation of U(IV)$_{fast}$, U(IV)$_{med}$, and U(IV)$_{slow}$.

Total U	Total U(VI)
◇ U(IV)$_{fast}$	○ U(IV)$_{fast}$
⊕ U(IV)$_{med}$	⊕ U(IV)$_{med}$
◆ U(IV)$_{slow}$	● U(IV)$_{slow}$

The effect of electron donor concentration on U(VI) reduction kinetics

Introduction

We hypothesize that the rate of U(VI) reduction can be controlled based on the amount of electron donor addition. Carefully controlled rates of U(VI) reduction may yield U(IV) precipitates that are resistant to reoxidation, and therefore more stable upon cessation of electron donor addition. We are conducting long-term column experiments to address the effect of electron donor concentration on the rate of U(VI) reduction.

Column preparation, characteristics, and run conditions

-Columns were "wet packed" with Oak Ridge Field Research Center Area 2 sediment in a 1:9 ratio of wet "seed" sediment to dried sediment.
-Average mass of sediment contained in each column was 52 g ± 3.
-Pore volume of each column was 26.4 ml (assuming 50% porosity).
-PIPES-buffered artificial groundwater (PBAGW) was pumped through columns at a rate of 0.05 pore volume/d.
-PBAGW feed was amended with 0 mM, 1 mM, or 10 mM ethanol

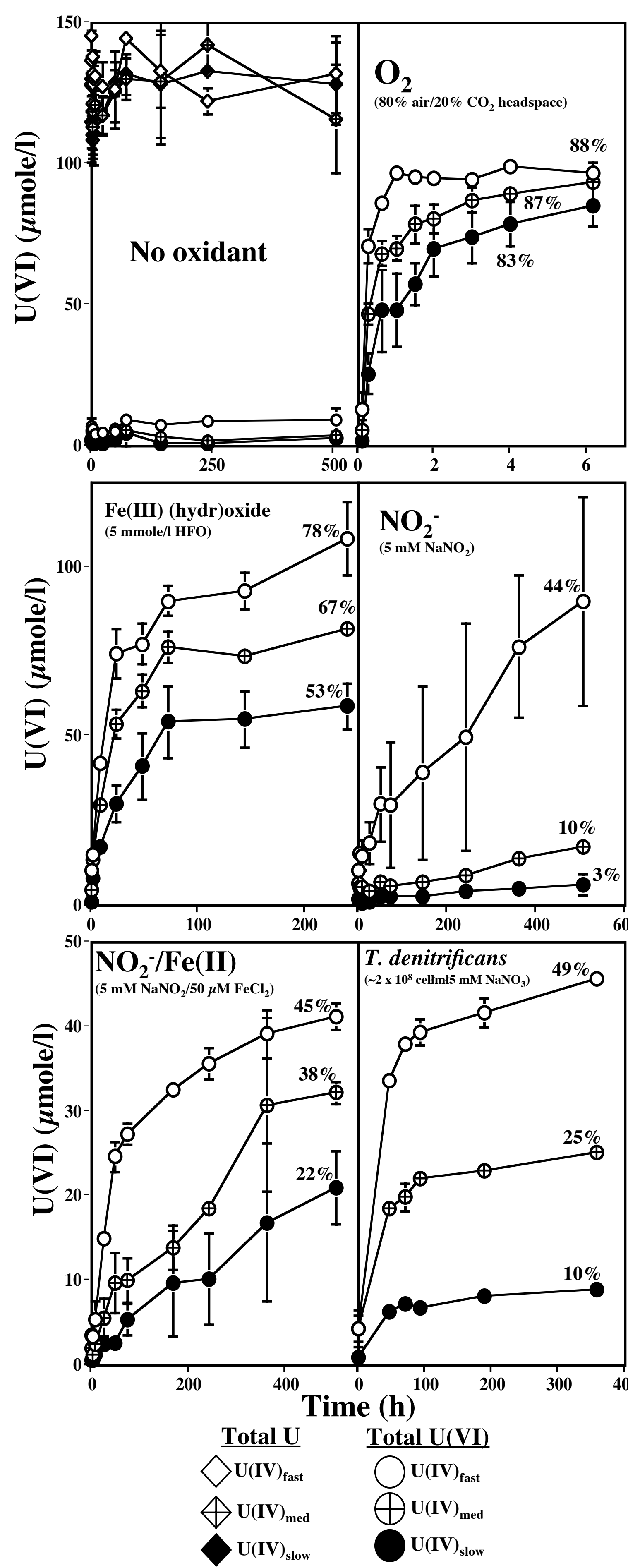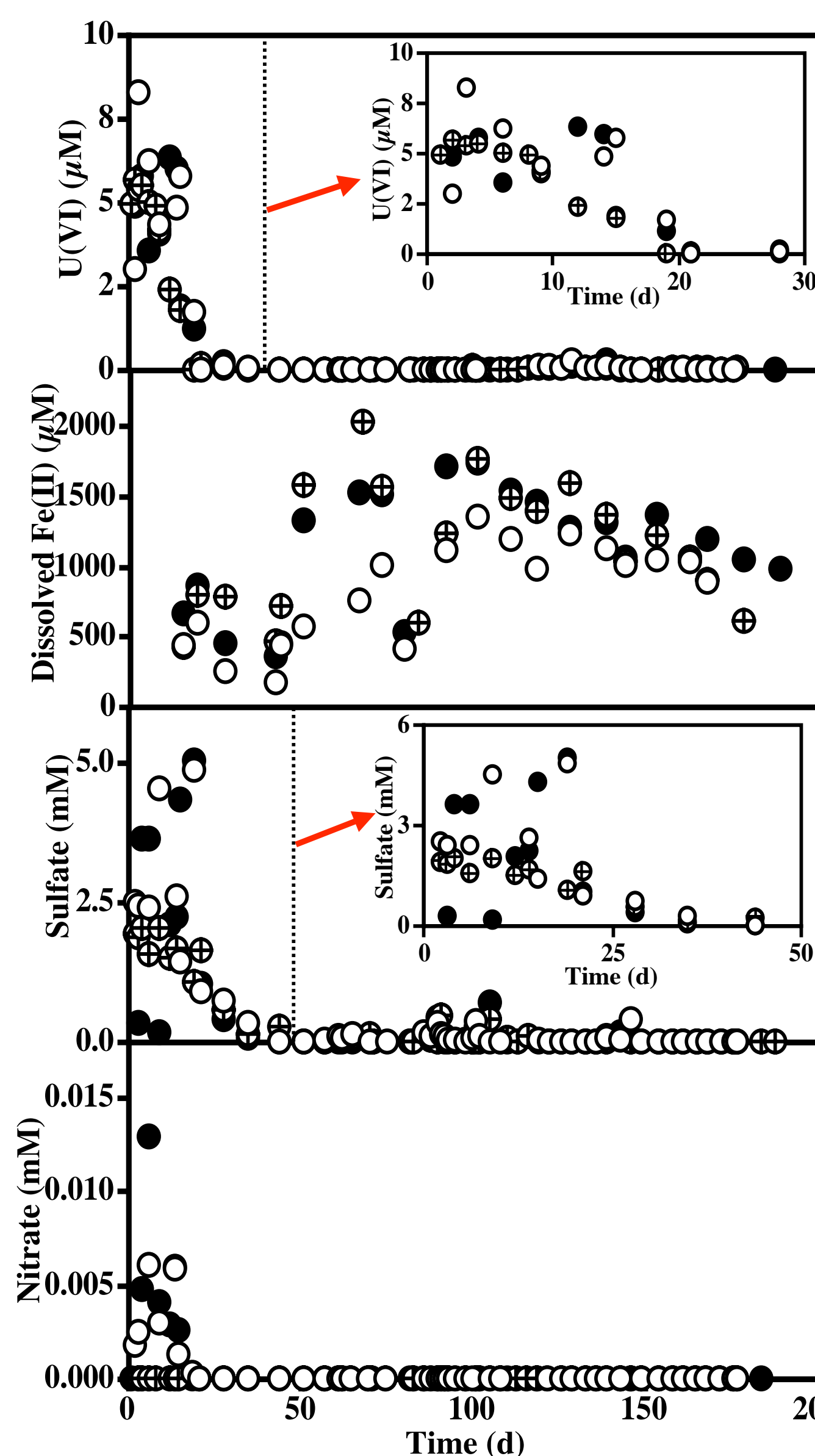| Components of PBAGW |
|---|
| 10 mM PIPES |
| 5 mM NaHCO₃ |
| 4.1 mM CaCl₂ |
| 1.1 mM MgCl₂ |
| 1.04 mM Na₂SO₄ |
| 0.65 mM NaNO₃ |
| 0.16 mM KCl |
| 0.1 mM NH₄Cl |
| 0.01 mM KH₂PO₄ |
| pH 6.5 |
| 85% N₂, 15% CO₂ headspace |

Figure 6. Effluent U(VI), soluble Fe(II), sulfate, and nitrate from Area 2 sediment columns receiving PBAGW amended with 0 mM (○), 1 mM (⊕) or 10 mM (●) ethanol.

Results and Discussion

-Ethanol additions have had little effect on nitrate, U(VI), Fe(III), and sulfate reduction
-U(VI) reduction concurrent with Fe(III) and sulfate reduction
-Sediments contain sufficient background organic matter to support extensive reduction of all TEAs
-More information on the effect of electron donor additions will be available upon complete depletion of background electron donor

Ongoing and future work

-Characterization of U(IV) precipitates produced at different rates
-U(IV) mineralogy (by electron diffraction analysis and XANES with collaborators at EMSL-PNNL and ANL)
-Cellular location of U(IV) precipitates (by TEM with collaborators at EMSL-PNNL)
-Determination of U(IV)-cellular material interactions (by EXAF with collaborators at ANL)
-Assess the rates of U(IV) reoxidation in FRC sediment column material upon completion of column experiments